

**ORGANIC-INORGANIC COMPOSITE
MEMBRANES FOR ELEVATED TEMPERATURE
OPERATION OF PEM FUEL CELLS IN THE
110°C-150°C RANGE**

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Operation of proton exchange membrane (PEM) fuel cells in the typical temperature range of 60°C- 80°C poses problems of carbon monoxide tolerance, slow kinetics of the oxygen reduction reaction and poor thermal management. These problems can be resolved by running PEM cells at elevated temperatures: 110°C-150°C. However, the proton conductivity of the standard Nafion membranes is only sufficient when the membrane is heavily hydrated, and operating the fuel cells above ~90°C tends to cause rapid water loss from the membrane leading to cell failure. We have previously demonstrated that addition of a few weight percent of certain metal oxide phases to a recast Nafion membrane in conjunction with pressurization of the fuel cell to three atmospheres overcomes this issue allowing stable cell operation in the indicated temperature regime. Under these conditions improved cell power output is observed and carbon monoxide concentrations of at least 1000ppm in the hydrogen feed stream can be tolerated.

This paper considers the chemical interactions that give rise to enhanced membrane performance at elevated temperatures along with reporting recent results that indicate composite membranes operate effectively at temperature above 100°C even under reduced humidity conditions. We further report that the composite strategy offers elevated temperature advantages when employed with polystyrene based membranes.

Although, it has been previously suggested that the metal oxide phase prevents the thermal dehydration of the membrane material, we find that water retention at elevated temperatures is related to the thermal and thermomechanical properties of the membrane material, not the physical properties of the aqueous phase. As shown in Figure 1, the addition of a metal oxide phase to Nafion is found to increase the glass transition temperature of this system. The self-assembly

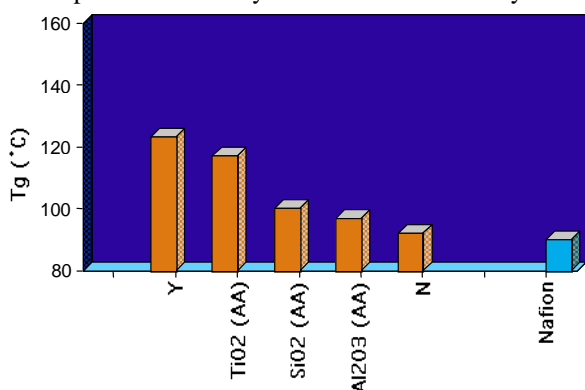


FIGURE 1: Dynamic mechanical analysis of Nafion composites showing the effect of various metal oxide phases on membrane glass transition temperature. (AA) indicates that the material was purchased from Alfa.

of the Nafion polymer into hydrophobic and water containing hydrophilic regions is considered key to its proton conductivity. Transition to the glassy states

destroys this self-organization, and thus is expected to lead to water loss, and reduced proton conductivity. Therefore, the retardation of the glass transition temperature by the metal oxide component serves to preserve the polymer morphology at elevated temperature that is essential to proton conduction. In addition, we believe that the metal oxide phase stabilizes the swelling and deswelling of the membrane as water production rates and evaporation vary due to changes in the current and thermal loads of the cell. Cell performance is strongly linked to the stress that the fuel cell fixture applies to the membrane material and its related strain response. Addition of selected metal oxides tends to stabilize these interactions.

Key to the interactions noted here is the finding that the type of metal oxide and the chemical composition of the metal oxide surface dramatically affect the membrane performance at elevated temperatures. In all cases, it is found that addition of a metal oxide phase slightly decreases the proton loading of the membrane. This leads to a slight decrease in membrane conductivity when measured outside of the cell, although the current-voltage response of the cell is unaffected when a select set of metal oxides is utilized. These observations indicate that the metal-oxide/polymer interface is the critical chemical element. In support of this conclusion, we find that chemical modification of the metal oxide surface, or a variation in metal oxide crystal structure (in the case of titania nanoparticles) impacts the current-voltage performance of the cell.

Titania nanoparticles having the anatase structure are found to give an extremely good in-cell response. Suggesting that it is the interaction between the polymer sulfonate groups and coordinately unsaturated interfacial

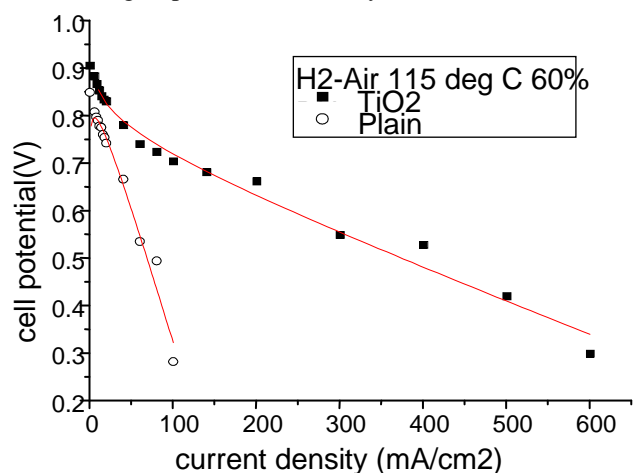


FIGURE 2: Current-voltage response of a recast Nafion film (□) vs. a titania composite film (■) under reduced humidity at 115°C operating temperature.

Ti(IV) sites that is the source of the observed stability. The improvement in cell response from such a system is shown in Figure 2 for a hydrogen- air cell operating at 115°C and 65% relative humidity. Cells of this type have been run for extended periods in the 130°C-140°C range with good stability and CO tolerance.

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